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Used Fuel Disposition Campaign

**Repository Science/THCM Near-Field
(Work Package FTLL11UF0332)**

***Level 4 Milestone (M4): M41UF033201
(LLNL input to SNL L3 Milestone)***

**FY11 DEVELOPMENT OF FULLY COUPLED REPOSITORY THCM SIMULATION
TOOLS REPORT**

- REVIEW OF RADIOLYSIS OF BRINES ON THE SURFACE OF A WASTE PACKAGE -

Lawrence Livermore National Laboratory

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Unit conversion:

$$1 \text{ Gy} = 1 \text{ J.kg}^{-1} = 1 \text{ m}^2.\text{s}^{-2} = 100 \text{ rad}$$

1. INTRODUCTION

The Used Fuel Disposition Campaign (UFDC) within the Department of Energy's Office of Nuclear Energy (DOE-NE) Fuel Cycle Technology (FCT) program has been tasked with investigating the disposal of the nation's spent nuclear fuel (SNF) and high-level nuclear waste (HLW) for a range of potential waste forms and geologic environments. A fully coupled thermal-hydrologic-chemical-mechanical-biological-radiological (THCMBR) performance assessment (PA) model would be extremely useful in understanding the long-term behavior of a repository.

Depending on the repository design, water may be present in the repository during various time periods in the form of either infiltrating ground water or atmospheric relative humidity. Infiltrating ground water is likely to be driven away from the emplacement boreholes by the thermal gradient from the waste package to a location within the host rock. However, as the temperature of the waste package cools, ground water containing dissolved species (e.g. Na^+ , Cl^- , Mg^{++} , Ca^{++} , SO_4^{--} , NO_3^- , NH_4^+) may return to the boreholes and contact the waste after some time. The elevated temperatures remaining at the waste package surface and EBS components will cause the water to evaporate, and therefore concentrate. Additionally, before ground water contacts the waste package, the high relative humidity potentially present in a drift or borehole may cause deliquescence of dust on the surface of the waste package. This can lead to the formation of small but significant amounts of highly concentrated brines that could potentially impact the integrity of the waste package.

While work is currently underway at other national laboratories within the Fuel Cycle Technology program to examine the role of radiolysis on the inside of the waste package and the effect on spent uranium fuel (Buck et al 2011), the risk posed to surfaces at the interface between the waste package outer surface and the engineered barrier from gamma radiolysis of complex brines should also be evaluated.

The materials used in the EBS depend on the geologic medium and the repository design. For example, a reference granite repository has a bentonite buffer in contact with the waste package, while a reference clay repository has a steel liner in contact with the high-level waste canister, and a deep borehole repository has a steel liner between the waste package and the host rock. In a reference salt repository, the waste package will be covered with a layer of crushed salt. At storage times before groundwater infiltration or dust deliquescence, the gamma radiation emitted from the waste package may impact the integrity of the EBS materials themselves, and this radiation damage of these EBS materials should also be evaluated.

The UFD R&D Roadmap identifies some areas in which radiolysis-related research deserves attention, in particular: radiolytic effects of brine solution with various types of cations and anions; characterization of temperature effects; accurate characterization of the effect of H_2O_2 caused by major changes in near-field

chemistry as a consequence of radiolysis; and THCM issues relating to gas generation from radiolysis. The four key factors in determining the chemical species formed from radiolysis are the:

- nature of the radiation
- total dose
- dose rate
- composition of the solution.

With regard to the latter factor, the interaction of radicals from water irradiation with other ions in solution, or the irradiation of the ions themselves can result in a myriad of radical anions. These anion radicals may be detrimental to the waste package material or EBS component, or they may *scavenge* harmful water radiolysis products, resulting in a more benign environment for the waste package or EBS material. The reactions between all of these atoms, ions and radicals must be understood to accurately assess the effect of radiolysis in complex brines on the integrity of the waste package material or EBS components.

This milestone report (M41UF033201) documents a literature review of relevant publications for gamma radiolysis occurring within a droplet of water on the outside of a waste package in a repository environment within the “Repository Science/THCM Near-Field” work-package (FTLL11UF0332) of the UFDC.

2. WASTE PACKAGE SURFACE DOSE

The surface dose for 3 example waste packages in 3 storage concepts was calculated by Radulescu at ORNL (2011).

Table 2-1 Maximum surface dose rates (rad/hr) with aging time for a HI-STAR 100 transport/storage cask containing 32PWR

Decay Time (yr)	Radial surface	Top surface	Bottom surface
0	315	2.0	250
10	2.75	0.03	9
20	2.22	0.02	2.8
40	1.17	0.08	3
100	0.023	0.001	0.05
200	0.010	0.0006	0.02
300	0.009	0.0005	0.018

Table 2-2 Surface dose rates (rad/hr) for a 4PWR waste canister in a reference clay repository (SKB design)

Decay Time (yr)	Radial surface	Top surface	Bottom surface
0	38,365	5,710	5,340
30	49.5	16.7	18.4
60	21	3.0	2.4
150	2.7	0.2	0.2
300	0.22	0.05	0.06
600	0.11	0.04	0.05
1×10 ³	0.10	0.04	0.04
3×10 ³	0.07	0.026	0.03
1×10 ⁴	0.04	0.012	0.015
2.5×10 ⁴	0.02	0.005	0.006
5×10 ⁴	0.02	0.004	0.005
1×10 ⁵	0.025	0.005	0.007
5×10 ⁵	0.017	0.004	0.003

Table 2-3 Surface dose rates (rad/hr) for a 1 assembly SNF waste canister in a reference deep borehole repository (SNL design)

Decay Time (yr)	Radial surface	Top surface	Bottom surface
0	1,000,000	209,500	1,125,000
30	4,600	840	5,750
60	1,300	220	1,400
150	170	26	160
300	5.3	0.9	5
600	0.2	0.04	0.2
1×10 ³	0.2	0.04	0.2
3×10 ³	0.17	0.03	0.14
1×10 ⁴	0.15	0.025	0.13
2.5×10 ⁴	0.18	0.04	0.17
5×10 ⁴	0.27	0.06	0.23
1×10 ⁵	0.37	0.07	0.34
5×10 ⁵	0.28	0.06	0.27

3 GAMMA RADIOLYSIS LITERATURE SURVEY

The available literature on radiolysis of chemical solutions can be divided into three categories, namely water (most simple system), salt solutions (binary salts in water), and complex brines (multiple salt components in water). Example literature describing the first two categories is given in section 3.1. Examples of radiolysis in more complex brines similar to those found in and around geologic repository environments are given in Section 3.2, below, in addition to possible effects on EBS materials.

3.1 SIMPLE CHEMICAL SYSTEMS

Many studies have been undertaken to understand both the thermodynamic and kinetic behavior of species generated from the radiolysis of simple water solutions (e.g. Allen 1954, Dainton 1947, Draganic and Draganic 1973, Hamill 1969, Pastina and LaVerne 2001). Water radiolysis is very well understood and is relatively easy to model.

Anbar and Neta (1967) compiled a list of specific bimolecular rate constants for the reactions of water radiolysis products with a variety of inorganic and organic compounds in aqueous solution. Buxton et al (1988) published a critical review of rate constants for reactions between hydrated electrons, hydrogen atoms and hydroxyl radicals in aqueous solutions in the presence of inorganic and organic compounds. These two articles are considered to be the most comprehensive collection of radiolysis rate constants.

Anbar and Thomas (1964) studied the pulse radiolysis of NaCl solutions and identified the product of the reactions to be Cl_2^- with a rate of production that was independent of oxygen concentration, first order in proton concentration from pH 3 to 0, and first order in chloride ion and hydroxyl radical concentrations. Additionally, Anbar, Meyerstein and Neta (1964) studied the radiolysis of aqueous halide solutions, namely KI, KF, NaCl, CsCl and NaBr with 7.8 krad/hr gamma irradiation in the presence of a nitrous oxide atmosphere.

Halide ion irradiation was examined using pulse radiolysis by Khorana and Hamill (1971), including iodide and bromide ions. LiCl radiolysis was investigated using pulse radiolysis by Woods et al (1975) in concentrated solutions up to 14 molar. Hadjadj et al (1982) studied the pulse and gamma radiolysis of concentrated LiI solutions, building on that of Pucheault et al 1979, confirming that I_3^- is formed with a yield that increases with LiI concentration, and the presence of I_2^- anion radicals occurs early in the process. These radical anions then recombine to form I^- and I_3^- .

Kelm and Bohnert (2000a) modeled the chemical reactions associated with gamma irradiation of NaCl solutions, noting 82 reactions leading to 12 intermediate products using the kinetic code MACKSIMA CHEMIST (Carver et al 1979). LaVerne and Tandon (2005) studied the production of H_2 and Cl_2 during radiolysis of calcium

and magnesium chlorides, and LaVerne et al (2009) studied NaBr solutions at millimolar concentrations.

Hyder 1965 measured the production of nitrite ions in neutral and alkaline solutions of nitrate with 1.8 Mrad/hr gamma irradiation over a millimolar to molar concentration range. In neutral solutions the reduction of NO_3^- by electrons and H atoms was observed. Additionally, in alkaline solutions the reaction involves O^- . Cook et al (2001) studied the reducing radicals present in nitrate solutions using pulse radiolysis, building on the work of Gratzel et al, with the formation of the NO_3^- radical and subsequent reaction with water to generate the NO_2 radical. Cook notes that the reaction with water involves O^- rather than H^+ .

Cunningham (1962) examined the free radicals present in gamma irradiated solid KNO_3 crystals and observed that radicals: NO_2^- , NO_2 , NO_3^- , NO_3 , NO and O_2^- were formed but were inconsistent with orbital and orientation requirements.

Daniels and Wigg (1967) studied gamma radiolysis in dilute NaNO_3 solutions as a function of dose, intensity, temperature, concentration, pH and a variety of scavengers. In neutral solutions, seven key reactions were identified, while in alkaline solutions six reactions were identified. It was also found that oxygen reacts with NO_3^- . Daniels and Wigg (1969) also investigated gamma radiolysis of concentrated (2.5 molar) NaNO_3 solutions at neutral and alkaline pH, noting that at high pH, yields were consistent with dilution solution work performed earlier. Katsumura et al (1991) examined the species formed from the irradiation of nitric acid, sodium- and lithium nitrates.

Wu et al (2002) examined the temperature dependence of carbonate radicals in NaHCO_3 and Na_2CO_3 solutions and identified $(\text{CO}_3)_2^{\cdot\cdot-}$ and $\text{H}(\text{CO}_3)_2^{\cdot-}$ radicals. Carbonate-containing groundwaters were also investigated by Nicolosi (1986). Kim and Hamill investigated the irradiation of halide and sulfate solutions, resulting in Cl_2^- and SO_4^- radical ions. LaVerne and Pimblott (1991) list many radiolysis scavenger reactions, including those for phosphate reacting with H atoms.

3.2 COMPLEX SOLUTIONS RELEVANT TO GROUND WATER AND NUCLEAR WASTE

Jenks and Walton (1981) studied the gamma radiolysis and subsequent H_2 and O_2 yields of salt-mine brines and hydrates, including the effect of temperature (30 to 182°C), NaCl , MgCl_2 and NaBr concentrations. They found that radiolysis increased in MgCl_2 solutions at higher temperatures and concentrations, and that radiolytic decomposition of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ occurred in the waters of hydration.

In 1983, Gray presented experimental research on the gamma radiolysis of groundwaters found near potential radioactive waste repositories. The salt brine groundwater contained mostly NaCl , but also included SO_4^{2-} , Ca^{++} , Mg^{++} , K^+ , Sr^{++} ,

HCO_3^- , Br^- , Fe^{+++} , Zn^{++} , $\text{B}(\text{BO}_3^{---})$, Li^+ and F^- which underwent 5.5 Mrad/hr irradiation. The results showed there is synergistic interaction between Cl^- and Br^- , and between Cl^- and SO_4^{--} , with minor constituents in the brine appearing to not have a significant effect on the gas pressure. No Cl_2 gas or its derivatives were found above 10 ppm in the samples analyzed.

Jain et al 1985 measured the effect of gamma irradiation on WIPP Brine A pH (containing Na^+ , K^+ , Mg^{++} , Ca^{++} , Sr^{++} , Cl^- , SO_4^{--} , HCO_3^- , Br^- and BO_3^{---}). In a series of tests, the initial solution pH values ranged from 7.4 to 0.3. After irradiation with 2.4 Mrad/hr, the pH values ranged from 7.1 to 5.3. The authors note that this "buffering" of pH by radiolysis could be a phenomenon beneficial to the prevention of waste package localized corrosion.

Bjergbakke et al 1989 examined the radiolytic products of natural waters (fresh water granite, sandstone underground, salt brine and sea water) via computer simulation using the CHEMSIMUL code (Rasmussen and Bjergbakke 1984). Constituent concentrations were typically on the order of millimolar with the exception of Na and Cl in salt brine and seawater (which were 0.5 - 5 molar). The authors identified 81 main reactions in the radiolysis of neutral aqueous solutions of inorganic ions, and added that organic constituents present in the waters are usually oxidized. This article appears to be one of the most comprehensive lists of complex brine radiolysis reaction constants.

Sunder and Christensen (1993) evaluated gamma irradiation of waters relevant to the nuclear fuel waste management program using the MACKSIMA CHEMIST model (Carver et al 1979). Their work considered only inorganic ions of Na^+ , CO_3^{--} and Cl^- in water in addition to organic materials such as formate and butanol. The authors list 36 reactions for a H_2O solution irradiated with gamma at 280 Gy/hr for 20 hours, plus an additional 11 reactions for a carbonate-containing solution, 46 additional species for solutions containing chloride.

Bounoil and Bjergbakke (2008) developed a comprehensive model to describe the radiolytic processes in a cement medium using CHEMSIMUL. The authors found that radiolysis was regulated by the inclusion of a calcium peroxide octahydrate precipitate between 0.1 and 0.2 Gy/s dose rates. The very high pH of cement pore solution promotes the radiolysis propagation.

Simonson and Kuhn (1984) predicted the amounts of radiolytically produced species in chloride-containing solutions that also contained iron to simulate overpack dissolution. The authors developed the RADIOL reaction kinetics code with a dose rate of 3.5 Mrad/hr. They included 39 reactions, and noted that a dynamic equilibrium is established where the concentrations of the minor constituents of the brine (Cl , H , HO_2^- , O_2^- , HO_2 and OH) are dictated by their reactions with the major constituents (H^+ , H_2O_2 , H_2 and O_2) and by their production rates, and that oxidizing species generated via radiolysis can initiate and propagate cathodic corrosion at the surface of the waste overpack.

Hull and Williams (1985) produced a selective annotated bibliography for the geochemistry of brine in rock salt and in temperature gradients and gamma radiation fields relevant to radioactive waste isolation in salt. The work is a good reference source for geochemical and radiolytic considerations in a salt repository.

Lewis and Reed (1986) studied the effects of gamma irradiation on waste package components in groundwaters. Specifically, they examined low carbon steel (A27) in the presence of a GR4 synthetic basaltic groundwater and the addition of methane. They noted that a dose of 10 krad/hr for one and two months increased the H_2 yield, and that increases in the organic carbon yield and sulfate ion concentration, and the corrosion rate of the coupons were observed in some of the tests. Additionally, the observed evidence for quenching of the radiolysis yields when basalt was added to the reaction vessel.

Glass et al (1986) studied the effects of 3.3 Mrad/hr gamma irradiation on the corrosion of austenitic stainless steels in tuffaceous rock pore water (J-13 well water). The authors observed corrosion potential shifts in the positive direction associated with the radiolytic induced production of H_2O_2 and OH radical. Their results also indicated that for 316L stainless steel in chloride media, the pitting corrosion potentials are unchanged by gamma irradiation.

Kelm and Bohnert (2000b) examined the effects of gamma irradiation at 100 Gy/hr to 1 MGy/hr on NaCl solutions, noting that H_2 , O_2 and ClO_3^- were present at various concentrations depending upon the pH and were dependent on the dose rate. Additionally, these authors noted that corrosion products (Ni, Cr, Fe and Mo) were observed in solutions of irradiated NaCl in contact with Hastelloy C-276.

Hua et al (2005) note that there is little information available in the literature on the effects of radiation on Alloy 22. However, Alloy C-4 is compositionally similar to Alloy 22 and the former has shown no enhancement of general, pitting or crevice corrosion when exposed to 100 rad/hr gamma irradiation in aggressive $MgCl_2$ brines (Shoesmith and King 1998).

4. RADIOLYSIS MODELS

Several radiolysis models are available and have been used in some of the publications listed above.

The MACKSIMA CHEMIST model can only accept one or two elements as inputs, with the third element needing to be added as a catalyst. More information on the model can be found in Carver et al (1979).

CHEMSIMUL (Rasmussen and Bjergbakke 1984) is a computer program for simulation of chemical kinetics. It can model complex reactions, in particular

radiolytic processes with pulse trains, or radiolysis from nuclear waste. It contains a translator module and a module for solving the resulting coupled nonlinear ordinary differential equations. There is also a module for verifying the mass balance. Heterogeneous processes can be simulated by so-called exchange equations. These and refreshable parameters are powerful tools for calculating many physico-chemical quantities, e.g. the ionic strength. Animated simulations with varying reaction rates are possible. The main computer platform for CHEMSIMUL is the Windows PC (XP or later). CHEMSIMUL comes in a modern Windows version with a Graphical User Interface (GUI). Also a classic version running in command mode (DOS and Linux) is available, using the same input and output format as the GUI version. CHEMSIMUL has successfully been tested on Linux under Wine from Redhat Enterprise 5 (taken from <http://chemsimul.dk/>, accessed July, 2011).

FACSIMILE (Chance et al 1977) has been used by other researchers involved in UFD and FCT work (Buck et al 2011). The model was originally developed to understand the radiolytic processes in gas-cooled nuclear reactors. More information on FACSIMILE can be found at <http://www.mcpa-software.com/facsimile/index.htm>, and in Buck et al 2011.

5. CONCLUSIONS AND DISCUSSION

While radiolysis models already exist to examine both the reactions and kinetics involved in a number of simple chemical systems (e.g. H₂O with Cl), the need for more complex solution radiolysis models is evident. In particular, radiolysis models should include all (or as many as possible) of the major ions found in either infiltrating water or dust deliquescence on the surface of a waste package. We propose a species database similar that presented in Buck et al 2011 (which includes water, carbonate and chloride reactants), but one also augmented to include additional reactions and kinetics more complex groundwater chemistries (e.g. including nitrate, bromide, iodide and trace inorganic and organic complexes). Such inclusions may require additional computational tools that can process more complex problems. However, at this time it does appear that codes such as FACIMILE and CHEMSIMUL would be capable of modeling the complex solution chemistry reactions and kinetics associated with radiolysis of brines, provided a database is adequately populated.

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